4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HN-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

5) Cautions

5.1 Routine preventative maintenance must be performed as scheduled and documented to assure optimum instrument performance. Typical routine maintenance includes inspection and replacement of sample delivery tubing. Maintenance performed shall be recorded in a dedicated instrument maintenance logbook. Refer to HN-EQ-004 for additional information.

6) Interferences

6.1 Spectral interferences may be caused by background emission, stray light from high concentration elements, overlap of spectral lines, and/or unresolved overlap of molecular spectra.

6.1.1 Subtracting emission backgrounds adjacent to the analyte wavelength may compensate for background emission and stray light.

6.1.2 Using alternate wavelengths or employing inter-element corrections may compensate for spectral overlaps.

6.2 Physical interferences may be associated with sample nebulization and transport as a result of sample characteristics. Variances in viscosity and surface tension can cause significant inaccuracy due to flow rate.

6.2.1 Physical interferences may be compensated for by dilution, using a high solids nebulizer, and/or improving the argon flow rate.

6.3 Chemical interferences may be associated with molecular compound formation, ionization effects, and vaporization effects. Chemical interferences, while not normally encountered, are highly dependent upon matrix characteristics and specific analytes.

6.4 Memory interferences may be encountered when analytes in a previous sample contribute to measured signal in a new sample.

6.4.1 Memory interferences may be compensated for by utilization of appropriate rinses and rinse times.

6.4.2 If memory interference is suspected, the sample must be reanalyzed after a sufficient rinse cycle.

6.5 High salt concentrations may cause suppression of analyte signal and impede interference tests.

6.6 In the presence of free sulfate, only minimal concentrations of barium will be solubilized.

6.6.1 Analysis of barium in samples having varying or unknown concentrations of sulfate should be completed as soon as possible following sample preparation.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.

7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HN-QS-009).

7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.

7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances
7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples shall be collected in 500 ml plastic containers and preserved to a pH of <2 with HNO_3.

8.2 Dissolved metal analyses shall be field filtered through a 0.45µ filter and preserved to a pH of <2 with HNO_3. Filtering should be completed in the field at time of sampling.

8.3 Sample pH should be verified at time of sample receipt and adjusted if necessary.

8.3.1 If adjusted at time of receipt, the sample shall be placed on hold, and stored for a period of 24 hours, after which the pH adjustment will be verified.

8.4 Soil samples should be collected in 4 oz wide mouth plastic containers.

8.5 Samples may be stored at room temperature. The holding time is six months for aqueous and solid matrices.

9) Equipment and Supplies

9.1 Thermo ICAP 6500 Duo

9.2 Various Class A volumetric flasks: 10.0, 25, 50, 100, 250, etc.

9.3 Variable volume pipettes: 1.0 and 5.0 ml.

9.4 17mm autosampler vials

10) Standards and Reagents

10.1 Argon gas supply: high-purity grade (99.99%).

10.2 Nitric Acid (HNO3): Concentrated HNO3 - trace metal grade.

10.3 Hydrochloric Acid (HCl): Concentrated HCl - trace metal grade.

10.4 De-ionized (DI) Water: Minimum Type II purity.

10.5 ICP CAL Standard #1 @ 20 mg/ml: Containing Ag, As, Be, Cd, Cr, Mn, Pb, Sb, Sr, Ti, Tl, V ; Al, B, Ba, Bi, Ca, Cu, Fe, Li, Mg, Mo, Ni, Se, U @ 100mg/L K, Na @ 2000mg/L; Th, Zn @50mg/L (Available from SCP Science)

Element	Concentration	Element	Concentration
Antimony (Sb)	20 mg/L	Magnesium (Mg)	100 mg/L
Aluminum (Al)	100 mg/L	Manganese (Mn)	20 mg/L
Arsenic (As)	20 mg/L	Molybdenum (Mo)	100 mg/L
Boron (B)	100 mg/L	Sodium (Na)	2000 mg/L
Barium (Ba)	100 mg/L	Nickel (Ni)	100 mg/L
Beryllium (Be)	20 mg/L	Lead (Pb)	20 mg/L
Bismuth (Bi)	20 mg/L	Antimony (Sb)	20 mg/L

Calcium (Ca)	100 mg/L	Selenium (Se)	100 mg/L
Cadmium (Cd)	20 mg/L	Strontium (Sr)	20 mg/L
Cobalt (Co)	100 mg/L	Thorium (Th)	50 mg/L
Chromium (Cr)	20 mg/L	Titanium (Ti)	20 mg/L
Copper (Cu)	100 mg/L	Thallium (Tl)	20 mg/L
Iron (Fe)	100 mg/L	Uranium (U)	100 mg/L
Potassium (K)	2000 mg/L	Vanadium (V)	20 mg/L
Lithium (Li)	100 mg/L	Zinc (Zn)	50 mg/L

10.6 ICP CAL Standard #2 Hf @50mg/L; S @200mg/L; Sn @ 20mg/L (Available from SCP Science)

Element	Concentration	Element	Concentration
Hafnium (Hf)	50 mg/L	Tin (Sn)	20 mg/L
Sulfur (S)	200 mg/L		

10.7 QCS-27 Standard Al, Ag, As, Be, Be, B, Cd, Ca, Cr, Co, Cu ,Fe ,Pb, Mg, Mn, Mo, Na, Ni, K, Sb, Se, Si, Sr, Tl, Ti, V, Zn @100 µg/mL (Available from High Purity Standards)

10.8 Interference Check Standard Solution A in µg/ml As 1000, Ba 300, Be 100, Cd 300, Cr 300, Co 300, Cu 300, Pb 1000, Mn 200, Hg 50, Ni 300, K 2000, Se 500, Tl 1000, V 300, Zn 300 (available from Peak Performance).

Element	Concentration
K	20000 mg/L
Se	500 mg/L
As, Pb, Tl	1000 mg/L
Ba, Cd, Cr, Co, Cu, Ni, V, Zn	300 mg/L
Mn	200 mg/L
Be	100 mg/L
Hg	50 mg/L

10.9 Interference Check Standard Solution B Ag @ 300 µg/mL (Available from Peak Performance)

10.10 Interference Check Standard 5 in µg/mL Al 1200, Ca 6000, Fe 5000, Mg 3000, Na 1000 (Available from Peak Performance)

Element	Concentration
Al	1200 mg/L
Ca	6000 mg/L
Fe	5000 mg/L
Mg	3000 mg/L
Na	1000 mg/L

10.11 Reporting Limit Stock Standard is prepared by adding the following amounts of single element standard, to a 200-mL volumetric flask, containing 5 mL concentrated HNO_3 and brought up to volume with reagent water. This standard is stable for 180 days when stored at room temperature (unless degradation is noted). Store in a polyethylene bottle and label with the Standard # (from the Standard Log Book), initials of the preparer, preparation date and expiration date.

Element	Volume of 1000 ppm Single Element Solution in 200mL.	Final Concentration (mg/L)
Aluminum	4.0 mL	20.0
Antimony	1.0 mL	5.0
Arsenic	0.40 mL	2.0
Barium	0.4 mL	2.0
Beryllium	0.16 mL	0.80
Bismuth	2.0 mL	10.0
Boron	4.0 mL	20.0
Cadmium	0.08 mL	0.40
Calcium	4.0 mL	20.0
Chromium	0.2 mL	1.0
Cobalt	0.2 mL	1.0
Copper	0.4 mL	2.0
Iron	2.4 mL	12.0
Lead	0.24 mL	1.2
Lithium	4.0 mL	20.0
Magnesium	4.0 mL	20.0
Manganese	0.2 mL	1.0
Molybdenum	0.8 mL	4.0
Potassium	20.0 mL	100.0
Selenium	0.8 mL	4.0
Silicon	4.0 mL	20.0
Silver	0.16 mL	0.8
Sodium	20.0 mL	100.0
Nickel	0.8 mL	4.0
Tin	0.8 mL	4.0
Strontium	0.2 mL	1.0
Titanium	0.8 mL	4.0
Thallium	0.8 mL	4.0
Vanadium	0.2 mL	1.0
Zinc	0.8 mL	4.0

10.12 Single Element Standards @ 1000 µg/mL Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn (Available from Environmental Express)

10.13 Second Source Single Element Standards @ 1000 µg/mL Bi, Ca, Li, Mg, Na, Sn (Available from VHG)

10.14 Low Level Metals Mix Standard 1 w/ As, Ba, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Sr, Tl, and V @ 0.5 mg/L and Be and Cd @0.2 mg/L and Al, Li, and Zn @1.0 mg/L and B @ 2.0 mg/L and Fe 8.0 mg/L and Mg, K, and Na @20 mg/L and Ca @ 50 mg/L. (Available from VHG ZALSLAB1103-100 or equivalent)

10.15 Low Level Metals Mix 2 w/ Sn @0.2 mg/Land Sb, Mo, and Ti @0.5 mg/L (Available from VHG ZALSLAB1104-100 or equivalent)

10.16 Initial Calibration Standards:

10.16.1 Calibration Standard (ICAL1) –

10.16.1.1 Add approximately 50 mL of reagent water with 5% HNO_3 and 3% HCl

10.16.2 Calibration Standard (ICAL2)–

10.16.2.1 Add 0.2 mL of reporting limit stock standard to 39.8 mL of calibration blank, mix well. Solution is stable for 48 hours.

10.16.3 Calibration Standard (ICAL3)–

10.16.3.1 Add 4 mL of High Calibration Standard to 36 mL of calibration blank, mix well. Standard is stable for 48 hours.

10.16.4 Calibration Standard (ICAL4) –

10.16.4.1 Add 8 mL of High Calibration Stock Standard to 32 mL of calibration blank, mix well. Standard is stable for 48 hours

10.16.5 Calibration Standard (ICAL5-High Standard Solution)

10.16.5.1 To a 100-mL volumetric flask containing calibration blank solution add 5 mL of ICP Cal Standard #1 (10.5), 5 mL of ICP Cal Standard #2 (10.6), and 0.5mL Si (10.12) and bring to volume with calibration blank solution and mix well. Standard is stable for 48 hours.

Element	(ICAL5)	(ICAL4)	(ICAL3)	(ICAL2)
Ag	1.0	0.20	0.10	0.004
Al	5.0	1.0	0.5	0.10
As	1.0	0.20	0.10	0.010
B	5.0	1.0	0.5	0.10
Ba	5.0	1.0	0.5	0.010
Be	1.0	0.20	0.10	0.004
Bi	5.0	1.0	0.5	0.05
Ca	5.0	1.0	0.5	0.10
Cd	1.0	0.20	0.10	0.002
Co	5.0	1.0	0.5	0.005
Cr	1.0	0.20	0.10	0.005
Cu	5.0	1.0	0.5	0.01
Fe	5.0	1.0	0.5	0.06
K	100	20	10	0.50
Li	5.0	1.00	0.5	0.10
Mg	5.0	1.0	0.5	0.10
Mn	1.0	0.20	0.10	0.005
Mo	5.0	1.0	0.5	0.02
Na	100	20	10	0.50
Ni	5.0	1.0	0.5	0.02
Pb	1.0	0.20	0.10	0.006
Sb	1.00	0.20	0.10	0.02
Se	5.0	1.0	0.5	0.02

Si	5.0	1.0	0.5	0.10
Sn	1.0	0.20	0.10	0.02
Sr	1.0	0.20	0.10	0.005
Ti	1.0	0.20	0.10	0.02
Tl	1.0	0.20	0.10	0.02
V	1.0	0.20	0.10	0.005
Zn	2.50	0.50	0.25	0.02

10.17 Initial Calibration Verification (ICV) – To a 100 mL flask containing calibration blank add 1.0 mL of QCS-27 Standard, 0.1 ml of second source Bi, Li, Sn and 0.25 mL of secondary source K, Na and Ca.

10.18 Initial Calibration Blank (ICB): reagent water with 5.0% HNO_3 & 3.0% HCl.

10.19 Interference Check Sample A (ICSA):

10.19.1 Add approximately 50 ml of calibration blank solution to a clean 100 ml Class A volumetric flask.
10.19.2 Add 2.5 mL of Interference Check Standard 5 solution.
10.19.3 Add 0.250 ml of Interference Check Standard Solution A and Interference Check Standard Solution B
10.19.4 Bring to a final volume of 100 ml.
10.19.5 This solution is stable for 48 hours

10.20 Intermediate Low Level Continuing Calibration Verification Standards:

10.20.1 Low Level Quality Control 3

10.20.1.1 Si and U intermediate standard To a 1 L volumetric flask add 20.0 mL of Si 1000 µg/mL and 0.5 mL U 1000 µg/mL bring to volume with reagent water with 5% HNO_3 and 1% HCl. Solution is stable for 6 months.

10.20.1.2 Cd and Sn Low Level Intermediate Standard To 100 mL flask add 50 mL calibration blank solution add 0.1 mL Cd 1000 µg/mL and 0.1 mL Sn 1000 and bring up to volume. Solution is stable for 6 months.

10.20.1.3 Tl, Se and Cu Low Level Intermediate Standard To 100 mL flask add 50 mL calibration blank solution and 0.1 mL Tl, Se and Cu @ 1000 µg/mL and bring up to volume with calibration blank solution.

10.21 Low Level Continuing Calibration Verification:

10.21.1 To a 50 ml standard vessel add ~25 mL calibration blank solution
10.21.2 Add 0.5 mL Si and U intermediate Standard (10.20.1.1)
10.21.3 Add 0.5 mL Low Level Metals Mix Standard 1 (10.14)
10.21.4 Add 0.5 mL Low Level Metals Mix Standard 2 (10.15)
10.21.5 Add 0.25 mL Tl, Se and Cu Low Level Intermediate Standard (10.20.1.3)
10.21.6 Add 0.4 mL Cd and Sn Low Level Intermediate Standard (10.20.1.2)

10.22 Continuing Calibration Blank (CCB):

10.22.1 Add 40 mL of calibration blank solution to a standard vessel

10.23 Continuing Calibration Verification (CCV):

10.23.1 Add 20 mL of calibration blank solution to a standard vessel
10.23.2 Add 20 mL of High Calibration solution and mix well
10.23.3 Solution is stable for 48 hours

Element	Concentration	Element	Concentration
Ag	0.50 mg/L	Mg	2.5 mg/L
Al	2.5 mg/L	Mn	0.50 mg/L
As	0.50 mg/L	Mo	2.5 mg/L
B	2.5 mg/L	Na	50.0 mg/L
Ba	2.5 mg/L	Ni	2.5 mg/L
Be	0.50 mg/L	Pb	0.50 mg/L
Bi	2.5 mg/L	Sb	0.50 mg/L
Ca	2.5 mg/L	Se	2.5 mg/L
Cd	0.50 mg/L	Si	2.5 mg/L
Co	2.5 mg/L	Sn	0.50 mg/L
Cr	0.50 mg/L	Sr	0.50 mg/L
Cu	2.5 mg/L	Ti	0.50 mg/L
Fe	2.5 mg/L	Tl	0.50 mg/L
K	50.0 mg/L	V	0.50 mg/L
Li	2.5 mg/L	Zn	1.25 mg/L

10.24 Internal Standard

10.24.1 To 100 mL flask add 50 mL DI water 0.1 mL HCl and 1.0 mL Sc and mix well. Solution is stable for 6 months.

10.25 Tuning Solution

10.25.1 To 500 mL flask add 250 ml DI with 5% HNO_3 and 1% HCL and 1 mL Zn 1000 µg/mL and bring to volume and mix well.

10.26 Rinse solution add 1000 mL DI water to 2 L container add 100 mL HNO_3 and 60 mL HCl and bring to volume with DI

10.27 Dilution Solution add 1000 mL DI water to 2 L container add 100 mL HNO_3 and 20 mL HCl and bring to volume with DI

10.28 Stock Spike Standards:

10.28.1 Metals Mix standard w/ Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Sn, Tl, V, and Zn @ 10 mg/L **and** Fe, K, Ca, Na, and Mg @ 1000 mg/L **and** B at 50 mg/L. (available from VHG ZALSLAB901-500 or equivalent)
10.28.2 Ti and Si Spike Stock @ 1000 ppm (available from Environmetal Express)

10.28.2.1 Single Element Working Spike Ti @ 10 mg/L and Si @ 50 mg/L.

10.28.2.1.1 Add 5 ml Ti and 25 ml Si Stock to 300 ml DI water in a 500 ml volumetric flask.
10.28.2.1.2 Acidify with 10 ml Nitric and 5 ml Hydrochloric acid.

10.28.2.1.3 Bring to final volume with DI water.

10.29 Stock Spiking Solution:

10.29.1 Soil Spike:

10.29.1.1 A 500 µl volume of each spike solution (10.28.1 and 10.28.2) is added to ~0.5 gram of solid after transfer to the digestion vessel. Following digestion (HN-MET-009), the digestate is brought to a final volume of 50 ml. Theoretical spike value is the 100 mg/kg for the trace metals, 1000 mg/kg for Ca/Fe/Mg/Na/K, and 25 mg/kg for B and Si.

10.29.2 Water Spike:

10.29.2.1 A 500µl volume of spike solutions (10.28.1 and 10.28.2) is added to the 50.0 ml volume of aqueous sample after transfer to the digestion vessel. Following digestion (HN-MET-010), the digestate is brought to a final volume of 50.0 ml. Theoretical spike value is 0.1 mg/L for the trace metals, 10 mg/L for Ca/Fe/Mg/Na/K, and 0.5 mg/L for B and Si.

10.30 All standards referenced in Sections 10.5 through 10.29 must be documented and referenced according to the guidelines documented in SOP HN-QS-001, *Reagent & Standard Tracking.*

11) Method Calibration

11.1 Initial Calibration

11.1.1 Analyze the calibration blank and standards (Section 10) using the parameters established in Section 12.1.3. Flush the instrument with the rinse solution between each standard.

11.1.2 Determine the calibration curve as a linear equation based upon instrument response versus standard concentration.

11.1.3 Correlation coefficient for the linear regression must be $\geq$ 0.998.

11.2 Initial Calibration Verification

11.2.1 Verify the initial calibration curve using a second source ICV standard (Section 10.16).

11.2.2 Acceptance Criteria:

11.2.2.1 Method 6010C

11.2.2.1.1 All analytes must fall within + 10% of the known concentration.

11.2.2.2 US EPA 200.7

11.2.2.2.1 All analytes must fall within $\pm$ 5% of the known concentration.

11.3 Continuing Calibration Verification

11.3.1 Analyze a CCB and CCV standard following the initial calibration verification and prior to sample analysis.

11.3.2 The CCB must be analyzed after every ten samples and at the end of the run. (Samples shall be defined as any analysis utilized in the completion of a Work Order such as field samples, method blanks, lab control samples, matrix spikes, etc.)

11.3.2.1 The CCB must exhibit analyte concentrations less than 3 times the IDL or less than the MDL (whichever is less).

11.3.3 The CCV standard must be analyzed after every ten samples and at the end of the run. (Samples shall be defined as any analysis utilized in the completion of a Work Order such as field samples, method blanks, lab control samples, matrix spikes, etc.)

11.3.3.1 CCV analytes must be $\pm$ 5% of the known value directly after calibration (EPA 200.7 only) then 10% throughout the run.

11.3.3.2 Measurement iterations ($\geq$4) must have a %RSD less than 3% for method 200.7 and iterations ($\geq$3) at <20% for 6010C.

12) Sample Preparation/Analysis

12.1 Start-up

12.1.1 Visual check of instrument:

12.1.1.1 Inspect auto-sampler tubing for deformation and replace as necessary.

12.1.1.2 Inspect spray chamber for drainage. If build up is noticed, clean.

12.1.1.3 Check torch and clean if necessary check nebulizer for any blockages

12.1.1.4 Record any maintenance in routine maintenance log book

12.1.1.5 Empty waste container

12.1.1.6 Inspect Argon gas flow. Ensure there is 90 psi in the argon supply and 70 psi to the instrument. If not, check gas supply and change as necessary.

12.1.2 Turn plasma on and let the instrument stabilize for approximately 15 minutes.

12.1.3 Following instrument stabilization, confirm basic instrument parameters are approximately set at:

12.1.3.1 RF power = 1150V

12.1.3.2 Auxiliary gas = 0.5 L/ min

12.1.3.3 Coolant gas = 12 L/min

12.1.3.4 Nebulizer gas flow = 0.50 L/min

12.1.3.5 Purge gas flow = Normal

12.1.3.6 Analysis pump rate = 40 RPM

12.1.3.7 Flash pump rate = 40 RPM
12.1.3.8 Analysis Mode = speed

12.1.4 When necessary adjust carrier gas flow rate according to manufacturer's instruction to obtain a definitive blue emission region of plasma above the load coil.
12.1.5 For all subsequent analysis, determine mean concentrations from a minimum of four iterations for EPA 200.7 and a minimum of three iterations for SW 6010C, at the optimum wavelength.

12.2 Inter-element Check Standards

12.2.1 Analyze ICSA at the beginning of each analytical run.

12.2.1.1 Recovery of target analytes must be ± 20% of the known value.

12.3 Sample Preparation

12.3.1 Aqueous samples requiring analysis for total metals must be prepared according the guidelines documented in SOP HN-MET-010, *Metals Aqueous Digestion.*
12.3.2 Solid samples must be prepared according to the guidelines documented in SOP HN-MET-009, *Metals Solids Digestion.*
12.3.3 Aqueous samples requiring analysis for dissolved metals do not require preparation. However, such samples shall be acid preserved in the field at time of sampling. If acid preservation has not been completed as a field activity, the laboratory shall preserve the samples appropriately and note the added preservation on the Sample Receipt Checklist (SRC).

12.4 Sample Analysis

12.4.1 Process samples using the same parameters as those used to establish and verify the calibration. Samples must be processed against the daily-established calibration curve.
12.4.2 Samples with analyte concentrations exceeding the linear dynamic calibration range must be diluted and be re-analyzed.
12.4.3 Samples with suspected matrix interference should be re-analyzed using a post digestion spike. If the post digestion spike does not meet criteria, analyze a serial dilution. If sample dilution does not alleviate the matrix interference, the method of standard additions should be used.

12.5 When internal standard response falls outside laboratory acceptance criteria of 70-130%, dilute the sample and reanalyze.

12.6 Typical Analytical Sequence:

12.6.1 Initial Calibration curve, minimum four standards and a blank
12.6.2 Initial Calibration Verification standards (once daily)
12.6.3 Initial Calibration Verification Blank (once daily)
12.6.4 Low-Level Initial Calibration Verification Standard (once daily)
12.6.5 Interference Check Sample A (ICSA)
12.6.6 Continuing Calibration Verification (CCV)
12.6.7 Continuing Calibration Blank (CCB)
12.6.8 Low-Level Continuing Calibration Verification Standard (LLCCV)
12.6.9 Method blank (one MB per preparation batch of 20 or less)

12.6.10 Laboratory Control Sample (one per preparation batch of 20 or less)
12.6.11 Client sample(s)
12.6.12 Matrix spike

12.6.12.1 For Method 200.7, prepare at a 10% frequency (one per every 10 samples)
12.6.12.2 For Method 6010C, prepare at a 5% frequency (one per preparation batch of 20 or less)

12.6.13 Matrix spike duplicate

12.6.13.1 For Method 200.7, prepare at a 10% frequency (one per every 10 samples)
12.6.13.2 For Method 6010C, prepare at a 5% frequency (one per preparation batch of 20 or less)

12.6.14 Continuing Calibration Verification Standard (CCV after every 10 samples)
12.6.15 Continuing Calibration Blank (CCB after every ten samples)
12.6.16 Low-Level Continuing Calibration Verification Standard (LLCCV after every 10 samples)
12.6.17 Client samples and batch QC samples (dilution test sample, PDS, MB, LCS and MS)
12.6.18 Continuing Calibration Verification Standard (CCV at end of analytical sequence)
12.6.19 Continuing Calibration Blank (CCB at end of analytical sequence)
12.6.20 Low-Level Continuing Calibration Verification Standard (LLCCV at end of analytical sequence)

12.7 Post-Digestion Spike (PDS) Addition:

12.7.1 An analyte spike added to a portion of a prepared sample should fall within the laboratory derived acceptance criteria.
12.7.2 The spike addition should be based on the indigenous concentration of each element of interest in the sample.
12.7.3 If the spike is not recovered within the specified limits, the sample should be diluted and reanalyzed to compensate for the matrix effect.
12.7.4 Results must agree to within 10% of the original determination.
12.7.5 The use of a standard-addition analysis procedure may also be used if the dilution technique proves inconclusive.

12.8 Dilution test:

12.8.1 If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank), an analysis of a fivefold dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected.

12.9 Method of Standard Additions (MSA):

12.9.1 When MS/MSD and PDS criteria are not met, the method of standard additions may be used to determine an accurate analyte level.
12.9.2 The MSA is an extension of the PDS where three PDS are performed on the same sample.

12.9.2.1 Ideally, the first PDS is spiked at approximately 50% of the estimated analyte concentration. The second PDS is spiked at ~100% and the third at ~150%.

12.9.3 The MSA analyte concentration is determined using linear regression using the four data points. An MS Excel spreadsheet calculation is employed to calculate results from MSA.

13) Troubleshooting

13.1 Refer to Thermo ICAP 6500 hardware manual for specific technical troubleshooting guidance.

14) Data Acquisition

14.1 Create a prep batch (as applicable) in LIMS.

14.2 The data acquired is transferred via QTEGRA™ to LIMS electronically. Calculations are performed by QTEGRA™ software and LIMS.

14.3 Analyst review of data is performed on the raw data and in LIMS prior to being validated.

15) Calculation, and Data Reduction Requirements

15.1 Calculation of Linear Regression Correlation Coefficient, r

$$r = \frac{\sum XY - \frac{\sum X \sum Y}{n}}{\sqrt{(\sum X^2 - \frac{(\sum X)^2}{n})(\sum Y^2 - \frac{(\sum Y)^2}{n})}}$$

Where:

X = individual values for independent variable
Y = individual values for dependent variable
n = number of pairs of data.
df = n-2

15.2 Calculation of the CCV % drift:

15.2.1 % Drift= [(Calculated conc - Theoretical conc) x 100] / Theoretical conc

15.3 The calibration curve versus sample response data produces the metal concentration in solution.

15.3.1 Equation for water samples:

$$Concentration(ug/L) = Sample\,\mathrm{Re}sponse(ug/L) x\ Dilution\ Factor\ (If\ Applicable)$$

15.3.2 Equation for soil samples (external calibration):

$$Concentration(ug/kg) = \frac{Sample\ Response(ug/L) x FV}{Weight\ of\ Sample(g)}\ x\ Dil.\ Factor\ (If\ Applicable)$$

Where:

FV = final volume of digestion, ml

15.3.3 If additional dilutions are used, the result must be multiplied by the total dilution factor.

15.4 QC Calculations: Calculate the percent recovery for various QC samples (MS, MSD, LCS) according to the following equations:

15.4.1 % Recovery, %R (for MS/MSD and LCS)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:

SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked)
SA = Spike Amount Added (mg/L or mg/kg).

15.4.2 % Recovery, %R (for standards and CCV)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:

SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.4.3 % RPD (for precision or replication evaluation)

$$\%RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:

SR_1 = Sample result for replicate 1.
SR_2 = Sample result for replicate 2.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Instrument Detection Limit (IDL)

16.1.1 IDL determinations should be determined quarterly and maintained with the instrument logbook.

16.1.2 IDL determinations are to be completed by averaging the standard deviations of seven measurements of a reagent blank, over a minimum of three non-sequential analytical runs.

16.2 Initial Calibration:

16.2.1 A calibration curve must be generated daily or whenever ICV/CCV fail to achieve acceptance criteria.
16.2.2 Acceptance Criteria:

16.2.2.1 Curve must be determined from a minimum of four standards and a calibration blank.
16.2.2.2 The regression coefficient "r" must be $\geq$0.998

16.2.3 Curve Failure Corrective Action:

16.2.3.1 Check standards and/or perform maintenance as necessary to correct problem.
16.2.3.2 Process a new initial calibration curve

16.3 Initial Calibration Verification (ICV):

16.3.1 Perform daily after generation of the initial calibration curve.
16.3.2 Acceptance criteria:

16.3.2.1 Must meet accuracy performance criteria of 90-110% as outlined in the applicable LIMS test code for Method 6010C.
16.3.2.2 Must meet accuracy performance criteria of 95-105% as outlined in the applicable LIMS test code for Method 200.7.

16.3.3 ICV Failure Corrective Action:

16.3.3.1 Evaluate condition and age of standards being used and/or perform any needed system maintenance.
16.3.3.2 Reanalyze the ICV and /or generate a new calibration curve as necessary to achieve acceptable calibration criteria.

16.4 Low-Level Initial Calibration Verification (LLICV):

16.4.1 Perform daily after generation of the initial calibration curve.
16.4.2 Acceptance criteria:

16.4.2.1 Must meet accuracy performance criteria of 70-130% as outlined in the applicable LIMS test code.

16.4.3 LLICV Failure Corrective Action:

16.4.3.1 Evaluate condition and age of standards being used and/or perform any needed system maintenance.
16.4.3.2 Reprocess the LLICV and /or generate a new calibration curve as necessary to achieve acceptable calibration criteria.

16.5 Continuing Calibration Verification (CCV):

16.5.1 The CCV must be run prior to sample analysis, after every 10 samples

(including QC samples), and at the end of the analytical sequence.

16.5.2 Acceptance Criteria:

16.5.2.1 For Method 200.7, the initial CCV for a sequence must meet accuracy performance criteria of 95-105%, based on a minimum of 4 replicates with a %RSD of <3%.

16.5.2.2 For Method 6010C and subsequent CCVs for Method 200.7, the CCV must meet accuracy performance criteria of 90-110%. The replicate %RSD must be <3% for method 200.7 and <20% for method 6020C.

16.5.3 CCV failure Corrective Action:

16.5.3.1 If the calibration does not meet the criteria, re-analyze the standard.

16.5.3.2 If subsequent analysis is outside of criteria, perform a new calibration curve.

16.5.3.3 All samples processed following the last acceptable CCV must be re-analyzed.

16.6 Low-Level Continuing Calibration Verification (LLCCV):

16.6.1 The LLCCV must be run prior to sample analysis, after every 10 samples (including QC samples), and at the end of the analytical sequence.

16.6.2 Acceptance Criteria:

16.6.2.1 Must meet accuracy performance criteria of 70-130% for analytes of a similar concentration, as outlined in the applicable LIMS test code.

16.6.3 LLCCV failure Corrective Action:

16.6.3.1 If the calibration does not meet the criteria, re-analyze the standard.

16.6.3.2 If subsequent analysis remains outside of criteria, perform a new calibration curve.

16.6.3.3 All samples of similar concentration (<CCV), processed following the last acceptable LLCCV must be re-analyzed.

16.7 Continuing Calibration Blank (CCB):

16.7.1 The calibration blank must be run prior to sample analysis, after every 10 samples (including QC samples), and at the end of the analytical sequence.

16.7.2 Acceptance Criteria:

16.7.2.1 All analytes must be less than three times the IDL.

16.7.3 CCB failure Corrective Action:

16.7.3.1 If the calibration blank does not meet the criteria, re-analyze the blank.

16.7.3.2 If subsequent analysis falls outside of criteria, perform any necessary maintenance and perform a new calibration curve.

16.7.3.3 All samples processed following the last acceptable CCB must be re-analyzed.

16.8 Linear Dynamic Range (LDR) Assessment

16.8.1 A LDR sample must be processed to assess linearity above the highest calibration standard.

16.8.2 Acceptance Criteria:

16.8.2.1 All analytes are must be within 10% of the true value of the LDR standard.

16.8.2.2 Sample concentrations greater than 90% of the LDR must be diluted and re-analyzed.

16.8.2.3 The LDR should be verified every 6 months (minimally) or whenever a modification in instrument hardware or operating conditions presents the potential for a change in the LDR.

16.8.3 LDR assessment failure Corrective Action:

16.8.3.1 If the LDR does not meet criteria for an analyte, no data for that analyte falling between the highest calibration standard and the LDR standard can be reported.

16.9 Blanks:

16.9.1 Rinse Blank(s)

16.9.1.1 Rinse blanks should be used to flush system components between blanks, standards, and samples.

16.9.1.2 Allow sufficient time to remove traces of the previous sample prior to new sample introduction.

16.9.1.3 Rinse blanks are not to be routinely run before QC samples. If carryover is an issue, rinse-out times may need to be addressed.

16.9.2 Calibration Blank(s)

16.9.2.1 See Section 16.7.

16.9.3 Method Blank(s)

16.9.3.1 A method blank must be processed with each batch of 20 or less samples of the same matrix and prepared on the same working shift.

16.9.3.2 Acceptance Criteria:

16.9.3.2.1 All analytes of interest should be less than one half the PQL and must be less than the PQL.

16.9.3.2.2 Method blank values exceeding the PQL indicate laboratory/reagent contamination and should be considered suspect.

16.9.3.2.3 Method blank values exceeding the PQL may be considered useable if:

16.9.3.2.3.1 The blank analyte concentration is < 5% of the sample analyte concentration,

16.9.3.2.3.2 less than 5% of the regulatory limit,
16.9.3.2.3.3 or less than 3 times the MDL (whichever is greater),
16.9.3.2.3.4 All associated samples are appropriately qualified, and Project Management notification/approval is completed.

16.9.3.2.4 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved QA project plan differs from the above.

16.9.3.3 Corrective Action:

16.9.3.3.1 If the method blank results do not meet the acceptance criteria above, then the laboratory must take corrective action to locate and reduce the source of the contamination.
16.9.3.3.2 All samples associated with the contaminated method blank must be reprocessed.
16.9.3.3.3 If samples cannot be reprocessed due to insufficient sample volume or other similar circumstances, a non-conformance must be documented in the data checklist for the analytical run. This must provide sufficient detail for project narration and to ensure all appropriate data flags are entered into LIMS.
16.9.3.3.4 Data reported with an associated contaminated method blank must be flagged with a "B".

16.10 Laboratory Control Sample (LCS):

16.10.1 The LCS must be processed with each batch of 20 or less samples of the same matrix and processed on the same shift.
16.10.2 Acceptance Criteria:

16.10.2.1 Must meet accuracy performance criteria as outlined in the applicable LIMS test code.

16.10.3 LCS Corrective Action:

16.10.3.1 If the LCS recovery does not meet acceptance criteria, the sample batch must be reprocessed.
16.10.3.2 If samples cannot be reprocessed due to insufficient sample volume or other similar circumstances, a non-conformance must be documented in the data checklist for the analytical run. This must provide sufficient detail for project narration and to ensure all appropriate data flags are entered into LIMS.
16.10.3.3 Data reported with a failed LCS must be flagged and narrated as to potential bias characteristics.

16.11 Low-level Quality Control Sample (LLQC):

16.11.1 The LLQC must be processed quarterly.
16.11.2 Acceptance Criteria:

16.11.2.1 Must meet accuracy performance criteria of 70-130% as outlined in the applicable LIMS test code.

16.11.3 LLQC Corrective Action:

16.11.3.1 If the LLQC recovery does not meet acceptance criteria, investigate the cause of the failure.

16.11.3.2 Reprocess the LLQC once the cause of the failure has been identified and corrected.

16.11.3.3 If a cause cannot be identified and corrected, spike LLQC at a higher concentration, process, and adjust PQLs accordingly.

16.12 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

16.12.1 A MS/MSD pair must be processed at a 10% frequency for Method 200.7 and at a 5% frequency for Method 6010C. MS/MSD samples must be of the same matrix and processed during the same working shift.

16.12.2 Acceptance Criteria:

16.12.2.1 Must meet accuracy and precision performance criteria as outlined in the applicable LIMS test code.

16.12.2.2 Recovery values should not be evaluated if the spike concentration is less than 25% of the parent concentration.

16.12.3 MS/MSD Corrective Action:

16.12.3.1 If the MS/MSD pair generates recovery values outside acceptance criteria, the deviation may be due to matrix effects. The LCS, internal standard recoveries, and calibration results must all be evaluated in order to determine if matrix interference is present. (Note that the MS/MSD are used to evaluate the matrix effect, not to control the analytical process.) If both the MS/MSD fall outside accuracy criteria for the same analyte, a matrix effect is suspected, assuming the LCS achieves accuracy criteria, and all internal standard recoveries are consistent.

As an example, if the matrix spikes exhibit low recovery but good precision, laboratory control samples exhibit acceptable accuracy, and internal standard recovery is consistent, the presence of matrix interference is probable.

16.12.3.2 If the MS/MSD pair generates inconsistent recovery values and/or suspect LCS values are present, laboratory error (and not matrix inference) is suspected.

As an example, if precision between the MS/MSD pair is poor and the LCS presents divergent results, the presence of laboratory error is probable.

16.12.3.3 If the MS/MSD fails acceptance criteria, the data must be evaluated for error or possible matrix effect.

16.12.3.4 If laboratory error is indicated, all associated samples must be reprocessed. If samples cannot be reprocessed due to limited sample volume or other similar circumstances, all reported values must be qualified and narrated as to potential bias or usability.

16.12.3.5 If matrix interference is indicated, associated samples may be reported with appropriate qualification and narration.

16.12.3.6 A non-conformance must be documented in the data checklist for either scenario and must contain sufficient detail for project narration and to ensure all appropriate data qualifiers have been entered into LIMS.

16.13 Internal Standards (IS):

16.13.1 Internal standards must be added to all samples and calibration standards. We utilize an automatic internal standard introduction system via a peristaltic pump.

16.13.2 Acceptance Criteria:

16.13.2.1 For samples processed according to USEPA 6010C and EPA 200.7, the IS results must be ≥70% and ≤130% of the original response in the initial calibration.

16.13.2.2 Analytical results associated with IS failures may not be reported.

16.13.3 IS failure corrective action:

16.13.3.1 If criteria are not met, the cause of the problem must be determined, corrected, and the samples re-analyzed.

16.13.3.2 The sample must undergo a five-fold (1+4) dilution to alleviate potential matrix interference. Note: Greater dilutions may be necessary for samples contributing significant matrix interference.

16.13.3.3 Samples undergoing a necessary dilution due to IS failure must be notated as such if the target analyte concentration falls below the reporting limit.

16.13.3.4 If samples cannot be re-analyzed, all associated results must be qualified as "Unusable".

16.14 Reported Analyte Concentration

16.14.1 Reported concentrations for applicable analytes must be reported from the least dilute analysis that achieves all required quality control parameters.

16.15 Interference Check Solution:

16.15.1 The interference check solutions must be processed at the beginning of each analytical sequence.

16.15.2 Acceptance Criteria:

16.15.2.1 Must meet accuracy performance criteria as outlined in the applicable LIMS test code.

16.15.2.2 All internal standard criteria must be achieved for the interference check solution analysis.

16.15.3 Interference Check Solution Failure

16.15.3.1 All samples associated with a failure of the ICS must be reprocessed.

16.15.3.2 If samples cannot be re-analyzed, all sample results must be qualified as unusable.

16.16 Dilution Test Check

16.16.1 If the sample analyte concentration is within the linear dynamic range and sufficiently high (>100 times the reagent blank), a sample dilution test should be completed at a five-fold dilution.

16.16.2 Acceptance Criteria

16.16.2.1 Must meet precision performance criteria as outlined in the applicable LIMS test code.

16.16.3 Dilution Test Failure

16.16.3.1 In the event of a dilution test failure, the sample must be closely inspected for indications of matrix interference.

16.16.3.2 A post digestion spike or standard addition should be completed on the failed sample to verify matrix interference.

16.17 Post Digestion spike requirements

16.17.1 One post digestion spike (PDS) must be completed for each batch of $\leq$ 20 samples.

16.17.2 The PDS should be spiked at the same level as the MS/MSD.

16.17.3 Acceptance Criteria

16.17.3.1 Must meet accuracy performance criteria as outlined in the applicable LIMS test code.

16.17.4 PDS Failure

16.17.4.1 If the spike is not recovered within the recommended limits, the sample must be diluted and reanalyzed.

16.17.4.2 The results of the diluted re-analysis must agree within $\pm$ 10% of the original determination.

16.17.4.3 If the PDS fails the various acceptance criteria, the sample should be processed using standard additions as detailed in Section 12.6.

16.18 Deviations and non-conforming events must be documented using a Nonconformance Corrective Action Report (NCAR) or as an Exception Report item on the laboratory review checklist. For mandatory QC failures (e.g. LCS), the NCAR must be submitted to the QA Manager via the NCAR database.

17) Data Records Management

17.1 All data is stored both electronically and hard copy for a minimum of 10 years.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard tracking, analyst must attempt to use one lot of reagents and standards with each batch.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used.

Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 The effective date of this SOP is the date in the header or last signature date, whichever is most recent.

17.6 Logbooks must be reviewed monthly by the department supervisor.

17.7 Logbooks must be reviewed quarterly by the QA Staff.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Demonstration of Proficiency:

19.1.1 Initial Demonstration of Proficiency

19.1.1.1 The laboratory must determine linear dynamic range, method detection limits, and evaluation of quality control samples prior to sample analysis by this procedure.

19.1.2 Routine Demonstration of Proficiency

19.1.2.1 Each analyst must demonstrate initial proficiency with sample preparation and/or analytical determination by generating 4 sets of data of acceptable accuracy and precision for target analytes in a clean matrix.

19.1.2.2 Each analyst must demonstrate ongoing proficiency annually with each sample preparation and/or analytical determination method by generating 4 sets of data of acceptable accuracy and precision for target analytes in a clean matrix or by passing performance in approved PT evaluations.

19.2 Method Detection Limits (MDLs) must be determined on an annual basis (at minimum) or whenever major modifications are performed on instrumentation (ex: change detector, auto-sampler, etc.).

19.3 On-going laboratory performance must be documented via performance evaluation studies and must be completed approximately every 6 months.

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
R01	10/1/14	CES	New SOP
R02	8/31/16	CES	Updated document review and retention criteria.
R02	8/31/16	CES	Updated 10.11 to 180 days.
R02	8/31/16	CES	Updated 10.16.1.1 and 10.18 to 3% HCl.
R02	8/31/16	CES	Updated 10.26 to 60ml HCl.

21) References and Related Documents

21.1 Environmental Protection Agency, "Method 6010C Inductively Coupled Plasma Atomic Emission Spectroscopy", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 3, February 2007.

21.2 U.S. Environmental Protection Agency, "Method 200.7, Inductively Coupled Plasma – Atomic Emission Spectroscopy," Methods for Chemical Analysis of Water and Wastes, Revision 4.4, 1994.

21.3 ALS Environmental Quality Assurance Manual, Revision (most current)

21.4 Table 20.1-A - ICP-AES Analyte Listing for SW 846-6010C

21.5 Table 20.1-B - ICP-AES Analyte Listing for Method 200.7

21.6 Table 20.2 - Calibration and QC Summary

Table 20.1-A

Analyte List: SW 846-6010C

Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

(Additional analytes may be added based upon appropriate performance data.)

Table 20.1-B

Analyte List: Method 200.7

Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

(Additional analytes may be added based upon appropriate performance data.)

Table 20.2
Summary of Calibration and QC Procedures for Method 200.7 & 6010C

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
Initial calibration (minimum 3 standards and a blank).	Daily initial calibration prior to sample analysis.	r > 0.998.	N/A.
Initial Calibration verification (second source).	Daily after initial calibration,	All analytes within ±5% of expected value for 200.7 / ±10% for 6010C.	Correct problem and repeat initial calibration.
Calibration blank.	Before beginning a sample run, after every 10 samples and at end of the analysis sequence.	No analytes detected > 3 x IDL.	Correct problem then analyze calibration blank and previous 10 samples.
Calibration verification (Instrument Performance Check Standard).	Before beginning a sample run, after every 10 samples and at the end of the analysis sequence.	All analytes within ±5% of expected value for 200.7 initial check then, ±10% for subsequent and 6010C. ≥4 replicates: 200.7 : CV = <3% 6010C : CV = <20%	Correct problem then repeat calibration and reanalyze all samples since last successful calibration.
Demonstrate ability to generate acceptable accuracy and precision using four replicate LCS analyses.	Once per analyst.	All analyte(s) within LIMS defined control criteria.	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria.
Method blank.	One per preparation batch.	No analytes detected > 3 x IDL.	Correct problem, re-digest and analyze method blank and all samples processed with the contaminated blank.
Interference check solutions (ICS-A).	At the beginning of an analytical run.	ICS-A: All non-spiked analytes < ½ MQL; Spiked analytes within ±20% of true value.	Terminate analysis; locate and correct problem; reanalyze ICS; reanalyze all affected samples.

Table 20.2
Summary of Calibration and QC Procedures for Method 200.7 & 6010C

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
LCS for the analyte.	One LCS per preparation batch.	All analytes within ± 15% of the expected value for 200.7 and +/- 20% for 6010C.	Correct problem, re-digest and reanalyze the LCS and all samples in the affected preparation batch.
Dilution test.	Each preparatory batch.	5X dilution must agree within ±10% of the original determination for analytes present at concentrations > 100x concentrations found in reagent blank.	Perform post digestion spike addition for failed analytes.
Post digestion spike addition.	When dilution test fails.	Recovery within 80%-120% of expected results.	Dilute the sample; reanalyze post digestion spike addition.
MS/MSD	5% frequency for 6010C, 10% frequency for 200.7.	QC advisory acceptance criteria, 70% - 130% for 200.7. 75% - 125% for 6010C.	Describe in Laboratory Review Checklist.
Internal Standards (ISs).	Every sample.	Sample IS intensity: *70-130% of initial calibration.*	Perform corrective action and/or dilution and reprocess all effected samples.
MDL study.	Performed Annually	Detection limits established shall be < the MQLs.	None.
IDL study.	Performed Quarterly	Average of standard deviation of reagent blank analyzed 7 times on at least 3 non-consecutive days.	None.
Low-level Initial Calibration Verification (LLICV)	Performed daily after Initial calibration	70%-130% of expected value spike at MQL.	Correct problem and repeat initial calibration.

Table 20.2
Summary of Calibration and QC Procedures for Method 200.7 & 6010C

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
Low-level Continuing Calibration Verification (LLCCV)	Performed before analysis of samples and after every 10 samples in the sequence.	70%-130% of expected value spike at MQL.	Correct problem then repeat calibration and reanalyze all samples of similar concentration since last successful calibration verification.
Low-level Quality Control Sample (LLQC)	One LLQC per quarter.	70%-130% of expected value spike at MQL. Carried through entire preparation process.	Correct problem, re-digest and reanalyze. If problem cannot be corrected, spike at a higher concentration and update PQLs accordingly.

PH MEASUREMENT

SM4500-H B/EPA 150.1/SW9040C/SW9045D

SOPID:	HN-WC-009	Rev. Number:	R09	Effective Date:	10/15/2017

Approved By: _____ Date: 9-19-17
Department Supervisor

Approved By: _____ Date: 9/19/17
QA Manager

Approved By: _____ Date: 9/19/17
Laboratory Director

Archival Date: _____ Doc Control ID#: _____ Editor: _____

PROCEDURAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR 24 ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

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PH MEASUREMENT

1) Scope and Applicability

1.1 This SOP provides guidance in the pH measurement of aqueous and solid samples.

1.2 The sensitivity limit for this method is 0.10 pH units.

1.3 This procedure may be used to provide pH in support of corrosivity characterization for hazardous waste testing. The following conditions must be met:

1.3.1 When corrosivity pH is requested, it is only applicable to liquid samples (section 12.3).
1.3.2 Method 9040C must be referenced as the analysis method.
1.3.3 If the pH is above 12.0, the sample must be measured at a temperature of 25±1°C.

2) Summary of Procedure

2.1 The pH probe is immersed in an aliquot of the sample or the sample extract and the resulting pH measured.

2.2 Meters utilize automatic temperature compensation (ATC) to correct for temperature variations in the sample.

2.3 This SOP is based upon and compliant with EPA 150.1, SM 4500H-B-11, SW846-9040C, SW846-9045D and SW846-9041-WST.

3) Definitions

3.1 DI = ASTM Type II laboratory distilled water.

3.2 Laboratory Control Sample (LCS): An analyte-free matrix spiked with known concentrations of all target analytes. This is used to evaluate and document laboratory method performance.

3.3 Sample Duplicate: A separate aliquot of sample, analyzed under the same analytical conditions as the parent sample, used to demonstrate the repeatability of the analysis.

3.4 Matrix: The component or substrate (e.g., surface water, groundwater, soil) which contains the analyte of interest.

3.5 Batch: A group of 20 or less field samples processed during the same analytical period (8 hours). Each analytical batch must contain at a minimum a lab control sample, and a sample duplicate.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HN-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

5) Cautions

5.1 Be knowledgeable of the MSDS information for each chemical used in the procedure.

6) Interferences

6.1 Oily or particulate matter adhering to the electrode and reducing the response may cause interferences. Gently wiping or rinsing the probe with DI water will usually correct this problem.

6.2 Samples with very low or very high pH may give incorrect readings. The use of a low-sodium electrode can minimize the error induced by extremely basic samples (pH >10). Readings outside the calibration range should be narrated to possible bias if no such probe is utilized.

6.3 Temperature effects caused by shifts in ionic equilibrium of the sample are eliminated through the use of a meter containing a temperature compensator.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

7.2.1 Read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.

7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HN-QS-009).

7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.

7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually

when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements, and

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Sample collection bottles – Plastic or glass, approximately 250 ml. These are purchased by the laboratory and meet EPA specifications for sample containers.

8.2 Samples should be analyzed in the field within 15 minutes of collection, whenever possible.

8.3 Preserve the samples with refrigeration at 4 ± 2 °C from the time of collection until analysis if a laboratory pH is required.

8.4 When samples are analyzed past holding time in the laboratory, they must be designated as such and appropriately narrated.

9) Equipment and Supplies

9.1 pH meter – Mettler Toledo Five Easy Plus

9.1.1 pH electrode – Glass combination w/ ATC connection (Mettler LE438 pH)

9.2 pH meter – SPER Scientific pH (SPER 860031)

9.2.1 pH electrode – Glass combination w/ ATC connection (SPER 850059P)

9.3 pH meter – VWR Symphony

9.3.1 pH electrode – Epoxy resin (Cole Parmer 27508-22)

9.4 Disposable plastic cups

9.5 Balance capable of weighing accurately to the nearest 0.01g

9.6 Stir bars

10) Standards and Reagents

10.1 Reagent water, Type II

10.2 Initial calibration pH buffers 1.68, 4.01, and 10.01 (available through commercial vendors).